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DETONATION PROPERTIES OF NITROMETHANE, DEUTERATED NITROMETHANE AND BROMONITROMETHANE †

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Liquid nitromethane (CH_3NO_2 — NM) is an important explosive material because of its chemical and physical simplicity. It has proved useful in studies of the chemistry and physics of initiation and detonation. We have experimentally investigated some of the effects on its properties due to replacing one of its hydrogen atoms with bromine (BrNM) and all its hydrogen atoms with deuterium (DNM). French workers have found that the failure diameter of DNM in glass is more than double that of NM.[1] We report critical diameters and diameter effect curves for NM, BrNM, and DNM in brass. In addition, detonation wave profiles were obtained by use of VISAR techniques. We recorded interface particle velocity profiles between the detonating liquids and polymethyl methacrylate (PMMA) windows. DNM has a larger critical diameter in brass than either NM or BrNM. DNM's diameter-effect curve lies below that of NM and above that of BrNM.

INTRODUCTION

Liquid nitromethane (NM) has been used in many basic studies to explore the fundamental behavior of explosive materials because of its physical and chemical simplicity. Much of what we know about the physics of initiating and detonating explosives is due to these studies. NM has probably been studied more extensively than any other explosive from a chemical standpoint. Notwithstanding this our knowledge of the chemical kinetics that occur in initiating and detonating NM is very limited.

The molecular composition of NM is CH_3NO_2. There are several possibilities for atom substitution for the hydrogen atoms. One is replacing one hydrogen with a bromine atom (BrNM). Initial experiments investigating the effect of this substitution on detonation phenomena were carried out at the New Mexico Tech. Another possibility is to substitute deuterium atoms for the hydrogen atoms-- producing DNM. French workers showed this has a surprisingly large effect on the critical diameter in Pyrex.[1]

Engelke et al.,[2-5] have hypothesized that the first step in the shock initiation and detonation chemistry of NM is the formation of the aci ion of NM (see Fig. 1). This is an ionization reaction which is enhanced in the high-pressure environment produced by a shock. Enhancement of the amount of aci present has been shown to affect both the detonation and initiation properties.

Since this is the case, one would expect that replacing the H atoms by other species would have an effect on the detonation properties. This paper discusses such effects when BrNM and DNM is detonated and compares the observed properties to

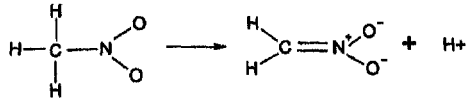

FIGURE 1. Formation of the aci ion of NM as proposed by Engelke et al. The B, P, and υ symbols over the arrow indicate that there is experimental evidence that chemical bases, high

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pressure, and ultraviolet light drive this reaction to the right.

those of ordinary NM. Large differences in critical diameter and diameter-effect curves are found. A companion paper concentrating on the properties of BrNM is also being given at this meeting.[6]

EXPERIMENTAL DETAILS AND DATA

Several types of experiments were completed in the course of this study. Critical diameter tests were done to define the minimum propagation diameter for the various materials in a brass tube. Detonation velocity tests were done in which the velocity of the detonating wave is precisely measured at a number of intervals as the wave propagates down a brass tube of a particular diameter. On some of the detonation velocity tests, a PMMA window with a thin aluminum mirror was put on the end of the tube and the interface particle velocity measured as a function of time to measure the reaction zone profile. A few gas gun experiments were completed on BrNM to study the shock initiation properties; they will not be discussed here.

Materials – The three different types of nitromethane were used as received from the supplier. CH_3NO_2 (99+% pure) and DNM (99 atom % D) were obtained from Aldrich; these were packaged in glass ampoules that were opened just before putting the DNM into the cylinders. BrNM was purchased from Lancaster Synthesis Inc.; it is technical grade BrNM. All the brass cylinders were 303? brass with 1 mm thick walls obtained from K & S Metals???.

Hugoniot Estimates – It was necessary to estimate the Hugoniots of the various liquids to help interpret the measurements. This was done by measuring the room condition sound speed and using the universal liquid Hugoniot[7]

$$U_s = C_0\{1.37 - 0.37\exp(-2u_p/C_0)\} + 1.62u_p$$

to predict the experimental unreacted Hugoniot; here U_s is the shock velocity, u_p is the particle velocity, and C_0 is the room condition sound speed. This equation has been shown to provide reliable unreacted Hugoniot estimates for essentially all the liquids for which are data available.

The measured sound speed and mass densities were: NM - C_0 is 1.32 mm/μs (1.125 g/cm^3), DNM – 1.27 mm/μs (1.183 g/cm^3), and BrNM – 1.16 mm/μs (2.006 g/cm^3). These Hugoniots have been used to estimate detonation parameters for these materials. In the case of NM and BrNM, gas gun experiments have produced data that support using Universal form estimates.

Critical Diameter Tests – These tests were done with brass tubes about 50 to 75 mm long. The tubes were filled with liquid explosive and then a detonator/booster used to initiate each tube. A steel dent plate was put at the end of the tube and sometimes a piece of copper next to the side of the tube. This is a go/no-go test as measured whether or not a dent occurs in the side or end plate. Based on this measurement, BrNM has a critical dia. Less than 0.8 mm and NM a critical dia. of 2.8? ±0.4 mm in brass.

The DNM tests gave confusing results because early critical dia. experiments showed a critical dia. of about 5.4 mm. However, longer tubes (150 to 225 mm) failed to propagate at 6.8, 7.2, and 10.2? mm but did propagate at 15.4? mm. Based on this DNM has a critical dia. of 12.8 ± 2.6 mm; this will be more carefully determined in further tests.

Detonation Velocity Tests – These tests were done with brass tubes about 150 to 225 mm long with pins along the tubes to record the wave progression down the tube. The liquid explosive in the tube was initiated with an SE-1 detonator and either a 12mm dia. by 12 mm long PBX9407 booster (tube dia. < 11mm) or a 25mm dia. by 25 mm long PBX9501 booster (tube dia. > 11 mm). One of the experiments is shown in Fig. 2.

Pins were put at either 10 mm or 20 mm increments along the side of the tube. As the wave came by each pin, the brass tube made contact with the pin and a voltage spike was measured by a digitizer to which the output of the electrical pulse forming circuit was hooked. With the spacing and time known accurately, the velocity in the tube can be determined to an accuracy of up to 2 m/s out of 6000 m/s. Early measurements were not this good but the technique was improved so this accuracy was obtained on some of the later tests. All tests were done inside a contained firing chamber where the temperature was between 18 and 21°C.

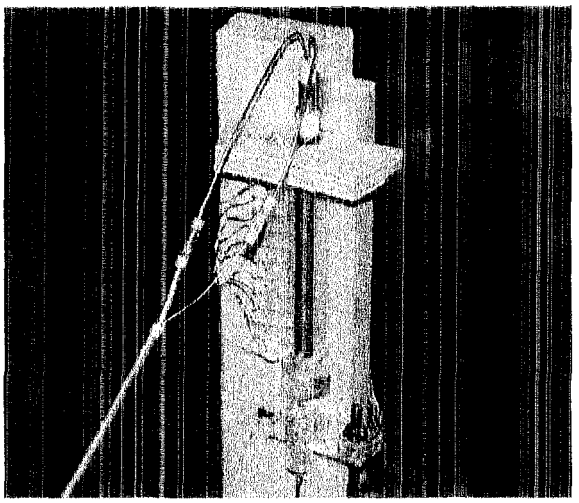

FIGURE 2. Detonation velocity rate stick showing detonator/ booster on top of the brass tube, 11 shorting pins down the left side, and a PMMA window and VISAR probe at the tube bottom.

Data from the experiments on NM, DNM, and BrNM is shown in Fig. 3 in the diameter effect curve plane, detonation velocity vs. reciprocal tube radius (1/R). The purity of the NM is apparently quite important because the two points we have for the 99+% NM came from a particular bottle. Two other points (at larger diameters) are not show because they didn't agree with these data and were from different bottles obtained at other times from Aldrich. This is being investigated at the present time and we feel that chemical analysis will have to be done on several bottles of a new batch and then they will have to be mixed together to get a rather large amount of NM that is quite pure. This is the reason Engelke has used "barrel" NM in the past on several studies; there is about 30 gallons of the material and it is not changing with time.

VISAR Reaction Zone Measurements – On some of the detonation velocity tests, a PMMA window with a thin aluminum mirror was put at the end of the brass tube and the interface particle velocity was measured. This setup is shown in Fig. 2 at the bottom of the tube. A thin Kapton sheet (8 mm thick) was glued between the vapor deposited aluminum and the NM. Interface particle velocity profiles from a NM and DNM experiment are shown in Fig. 4. There are two profiles for each experiment because there were two Valyn VISARs[8] on each experiment set at different fringe constants.

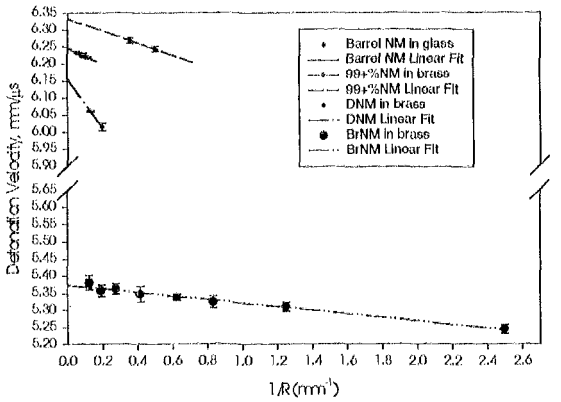

FIGURE 3. Diameter effect curves for NM, DNM and BrNM. Fit lines stop at the critical diameter.

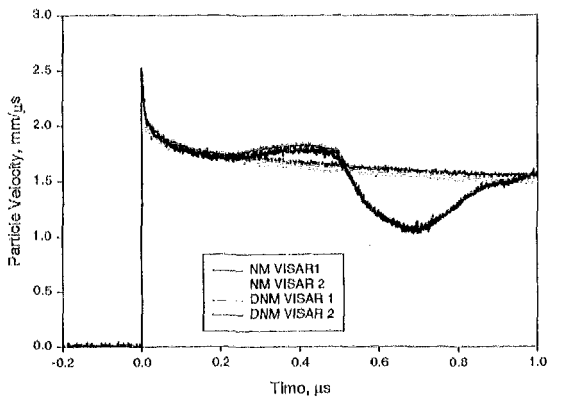

FIGURE 4. VISAR interface particle velocity measurements for NM and DNM. There were two VISARs on each experiment.

The fact that the two profiles lie essentially on top of one another is evidence that the measurements are correct. Time resolution of the VISAR measurements is about 2 ns.

DISCUSSION OF RESULTS

As shown in Fig. 3, the infinite-medium detonation velocity of normal and deuterated NM are significantly different. The values being $D(\infty) = 6.335 \pm ?$ and $D(\infty) = 6.160 \pm ?$for normal and deuterated NM, respectively; i.e., the value for DNM is ca. 175 m/s lower than that of normal NM. Since the infinite-medium velocity intercept corresponds to a one-dimensional (1-D) detonation, its value is independent of the chemical kinetics and is dependent on the heat of detonation, provided the ZND detonation model is correct. It is, therefore, of interest to examine this measured difference in

velocity more closely and to try to understand it in terms of changes in the heat of detonation.

The changes in the heat of detonation that occur from deuteration are due to: (1) the increased molecular weight and (2) changes in the molecular vibrational levels due to the increased mass of the hydrogen nuclei. Using the ZND result for $D(\infty)$, i.e., $D(\infty)^2 = 2q(\gamma^2-1)$, where q is the heat of detonation per gram and γ is an equation of state parameter, one finds that a small fractional change in q produces an accompanying change in $D(\infty)$ given by $\Delta D(\infty) = D(\infty)[\Delta q/2q]$. It is straight forward to show that $[\Delta q/2q] = -3/[2(m_0 + 3)]$ due to NM being deuterated; here m_0 is the molecular weight of NM. Since $m_0 = 61$ and $D(\infty) = 6335$, one finds that $\Delta D(\infty) = -148$ m/s due to the change in molecular weight.

The question of the change in q due to the shift in vibrational levels was addressed by doing PM3 quantum chemical calculations using Gaussian-98.[9] The only important detonation product whose vibrations are altered by deuteration is water and ca.1.48 mol of water are produced by the detonation of 1.00 mol of NM. Our calculations on NM, DNM, H_2O, and D_2O indicate that ca. 0.019 kcal/g less energy is released by DNM than from NM due to vibrational effects. By a calculation similar to that outlined above, one finds that the corresponding change in $D(\infty)$ due this change in q is -48 m/s.

Thus, a total reduction in $D(\infty)$ of ca. -196 m/s is predicted when NM is deuterated. This value is in reasonable agreement with the measured value of -175 m/s obtained from the experiments.

It should be pointed out that the slope of the diameter-effect curve, at large tube diameters, is often said to be related to the reaction-zone thickness. Following this thinking, the slopes of the diameter effect lines in Fig. 3 indicate that the reaction zone in the DNM would be longer and the one in BrNM shorter than that of NM. To investigate this we completed experiments to measure the reaction zone profile of all three materials. We were unsuccessful in measuring the BrNM reaction zone because it is apparently too short to be measured by our VISARs, i.e., it is less than 2 or 3 ns. However, the VISAR measurements shown in Fig. 4 for NM and DNM show a reaction zone with a spike that is about what was expected based on the unreacted Hugoniots and detonation velocity for each material. Close scrutiny of the records indicates that the DNM curve is slightly above the NM curve during the first 30 ns, This is an indication that the reaction zone for DNM is slightly longer; than that of NM. Higher time resolution VISARs would be very helpful and are planned for future experiments. The reaction zone profile for NM is similar to earlier measurements and indicates a 10 to 15 ns long reaction zone.

This study shows a striking effect in NM of substitution for the H atom Although the effect on detonation velocity can be accounted for, the effect on the critical diameter and reaction zone is somewhat surprising and more work will have to be done to understand this. This work is continuing and is expected to produce more understanding about the chemical reactions taking place in the detonation process of NM.

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